Evidence for Critical Double Points in Blends of Polystyrene and Poly(o-chlorostyrene)

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Published in:
Macromolecules

DOI:
10.1021/ma00237a008

Publication date:
1983

50 wt % PPO. A summary of results is shown in Figure 12. It is clear that under these conditions, the incorporation of the plasticizer is indeed much less effective in varying the SI than for the 20 wt % PPO blend. From these data, it can be anticipated that a peak in SI similar to that observed with the 20 wt % PPO blend would be observed at DOP concentrations higher than those that can be used in our laboratory. Thus, once again the predictions of the damped Debye lattice model have been observed experimentally for the PPO–PS system.

Conclusions

We have used the behavior of the compatible polystyrene–poly(2,6-dimethyl-1,4-phenylene oxide) blend in the primary transition region to investigate the credibility of the damped Debye lattice model. We have studied the properties of blends that contained various amounts of PPO and have also investigated the behavior of several of these blends plasticized with dioctyl phthalate.

On the basis of information concerning the enthalpy of mixing, the excess density of mixing, polymer backbone structure, and the glass transition temperatures of blends of these two polymers, we have deduced how intra- and intermolecular interactions (force constants) vary with the amount of PPO in the blends. Using this information, we have shown that the damped Debye lattice model qualitatively predicts many aspects of the behavior of PS–PPO blends in the primary transition region. Experimentally, all of these predictions were found to be correct. This being the case, we may conclude that the damped Debye lattice is indeed a very powerful model to use in rationalizing viscoelastic behavior in the primary transition region. Fundamentally, these results show that interchain interactions, which can conveniently be disregarded in solution, are of primary importance in bulk and the influence of these interactions on viscoelasticity relaxation in the primary transition region is often profound.

Acknowledgment. This work was supported by Grant No. DAAG 29-79-C-1067 from the U.S. Army Office of Scientific Research.

Registry No. PS, 9003-53-6; PPO, 24938-67-8; 2,6-dimethylphenol homopolymer, 25134-01-4.

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Evidence for Critical Double Points in Blends of Polystyrene and Poly(*o*-chlorostyrene)

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ABSTRACT: Theoretical and experimental evidence is put forward to prove that both UCST and LCST behavior can be found in blends of polystyrene and poly(*o*-chlorostyrene). Vapor sorption results combined with known results of heat of mixing experiments lead to the conclusion of the rather uncommon UCST behavior. Existing data of T_g measurements show that the PS/PoClS system is extremely sensitive to a small change in molar mass. A decrease in molar mass of PS of less than 4000 transforms an only partially miscible system into a system that is miscible throughout the entire experimental temperature range from 150 to 400 °C. The enhanced sensitivity is shown to be related to the existence of a critical double point in the system under consideration and as such provides additional proof for the existence of both UCST and LCST in PS/PoClS blends. The last section is devoted to a model calculation, using Flory's equation of state theory. It shows in a most convincing way the enhanced sensitivity near a critical double point.

Soon after the discovery of the LCST phenomenon in polymer solutions, Flory and co-workers formulated a mean field theory that could explain this behavior.[1,2] The so-called equation of state theory shows that for nonpolar polymer solutions one should expect phase separation upon heating and upon cooling. A lower critical solution temperature (LCST) is associated with the first one and an upper critical solution temperature (UCST) with the latter one. A UCST was of course well-known and could be explained by the Flory–Huggins theory.[3-5] In order to explain the LCST behavior, it is essential to take the differences in equation of state properties of both pure components into account. Based on this viewpoint various other theories have been developed, all capable of explaining at least qualitatively the occurrence of an LCST.[6,7]

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0024-9297/83/2216-0381$01.50/0

Some years after the formulation of the equation of state theory, McMaster applied it extensively to mixtures of high molar mass polymers.[8]

According to the existing theories, the Gibbs free energy of mixing consists of three contributions: the combinatorial entropy of mixing, the exchange interaction, and an equation of state or free-volume term. The latter one is in general unfavorable for mixing and increasingly so at higher temperatures. For a mixture of two polymers the combinatorial entropy of mixing will be very small and specific interaction, resulting in a negative exchange interaction contribution to the free energy of mixing, will usually be a prerequisite for mixing. Only if the free-volume contribution is very small can a small positive exchange interaction be tolerated. In that case, as shown by McMaster, the system can exhibit both UCST and LCST behavior. Generally, however, only LCST will be observed, as is experimentally verified for many systems.[27]

The above arguments indicate that in order to observe UCST and LCST behavior one should consider polymer blends of polymers that are very much alike. A possible example is given by the pair polystyrene (PS) and poly(*o*-chlorostyrene) (PoClS). Ryan[9] studied PS/PoClS blends as a function of the molar mass of polystyrene. The phase behavior of the polymer blends was investigated with differential scanning calorimetry to measure the T_g of the blends after the blends were annealed at a series of temperatures between 150 and 400 °C. The result of these annealing studies was that the poly(*o*-chlorostyrene) with a molar mass of 100 000 blended with a polystyrene of molar mass greater than or equal to 30 400 could be phase separated. The same poly(*o*-chlorostyrene) blended with a polystyrene with a molar mass equal to or less than 26 700 exhibited one T_g and could not be phase separated. A change in the molar mass of polystyrene of less than 4000 results therefore in the creation of a temperature range in which both components are miscible of more than 250 °C.

In addition to this, Ryan[9] also measured the mixing enthalpies for these polymer–polymer pairs at 35 and 68 °C. The direct determinations are, of course, impossible, but the required parameters can be obtained from differential heat of solution measurements.[9,10] In this way, small but nearly always positive values for the enthalpies of mixing were found. Moreover, the molar mass of polystyrene did not have any significant influence on these values.

Additional information obtained by vapor sorption measurements is presented in the first section of this paper. The amount of vapor sorbed is related to the Flory/Huggins parameter. When these vapor sorption measurements are performed for each of the pure components and for the blend, the Flory/Huggins parameter χ_{12} of the two polymers in the blend can be found. The main result is that χ_{12} is small and positive for two of the three blend compositions investigated.

In order to explain his experimental results, in particular the remarkable sensitivity of the phase behavior to a small change in molar mass, Ryan[9] postulated that blends with the higher molar mass polystyrene have an hourglass-type phase diagram; that is, the upper critical solution temperature UCST and the lower critical solution temperature LCST have merged. The temperature of this merger was suggested to be about 550 K. The blends with the lower molar mass polystyrene are single-phase systems because as the molar mass of the polystyrene decreases, the UCST decreases and the LCST increases to the extent that both critical points are beyond experimental detection. Even in that case, however, the change in UCST and LCST due to the small change in molar mass of polystyrene is far larger than ever reported before, experimentally as well as theoretically.

We will show that the vapor sorption results combined with the enthalpy of mixing results of Ryan indeed clearly point to the existence of both an upper and a lower critical solution temperature in PS/PoClS blends. For a suitable choice of the molar masses the critical points will coincide in a so-called critical double point. We will show that, starting from a situation like that, a small decrease in molar mass of one or both components results in the creation of a large temperature range in which both components become miscible. The positions of both the LCST and UCST are very sensitive to a small change in molar mass. It is this enhanced sensitivity, typical for polymer systems near or at a critical double point, that is responsible for the observed phase behavior.

In the last section, we present some model calculations based on Flory's equation of state theory. They show that a small change in molar mass can easily raise the LCST by 150 °C and lower the UCST by a similar amount, as long as the starting point is a system near or at a critical double point.

Experimental Section

Polystyrene. Two different molar mass samples of polystyrene having narrow distributions were used. The lower molar mass sample was obtained from Pressure Chemical Co. The polystyrene is atactic batch 41220. It was prepared by anionic polymerization. The characterization data was provided by Pressure Chemical Co. The number-average molar mass as determined by membrane osmometry is $\bar{M}_n = 15\,000 \pm 6\%$. The weight-average molar mass as determined by light scattering is $\bar{M}_w = 20\,400 \pm 6\%$. The polymer was used as received without further purification.

The higher molar mass sample was obtained commercially from Goodyear Chemicals. It is anionically polymerized atactic polystyrene sample CDS-S-6. The characterization data was provided by Goodyear. The number-average molar mass as determined by membrane osmometry is $\bar{M}_n = 80\,800$, as determined by GPC $\bar{M}_n = 75\,300$. The weight-average molar mass as determined by light scattering is $\bar{M}_w = 82\,900$, as determined by GPC $\bar{M}_w = 82\,100$. The polymer was dissolved in toluene, filtered through a very fine sintered glass funnel, precipitated into methanol, and then dried under vacuum at 80 °C for several days before being used.

Poly(*o*-chlorostyrene). The polymer was synthesized by free-radical polymerization using the same technique as Ryan.[9] The number-average molar mass as determined by GPC was $\bar{M}_n = 77\,700$. The weight-average molar mass as determined by GPC was $\bar{M}_w = 169\,000$. The polymer was then fractionated with a preparative GPC, constructed at the University of Connecticut, Storrs, CT, in the laboratories of Dr. Julian Johnson. The fraction used in the vapor sorption measurements had a number-average molar mass $M_n = 100\,500$ and a weight-average molar mass $M_w = 147\,100$ as determined by GPC.

Decahydronaphthalene. Decahydronaphthalene, obtained from Fisher Scientific Co., was refluxed over $LiAlH_4$ for 3.5 h at atmospheric pressure and 180 °C. It was then distilled under partial vacuum at 83 °C.

Film Preparation. Films containing PS, PoClS, and their mixtures were cast from methylene chloride solution onto aluminum pans. Initial polymer concentration in methylene chloride was about 4%. The ratio of PS to PoClS is on weight basis. This technique provided a sample that was thin, on the order of 0.1 mm. The solvent was allowed to evaporate at room temperature for several hours. The films were then dried under high vacuum 10^{-4} mmHg at 80 °C for several days in an abderhalden drying tube. The absence of residual solvent was confirmed by a constant glass transition temperature.

Vapor Sorption Measurements

Vapor sorption technique is used to study the thermodynamic properties of polymer–solvent systems and

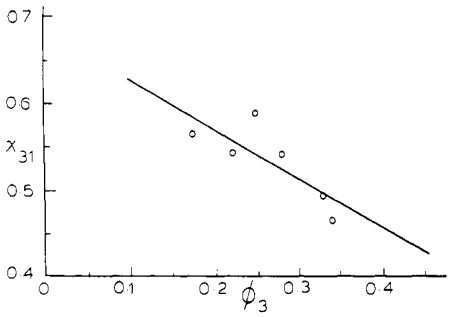

Figure 1. Concentration dependence of the χ parameter for the system $C_{10}H_{18}$/PS(15 000) as measured by vapor sorption experiments.

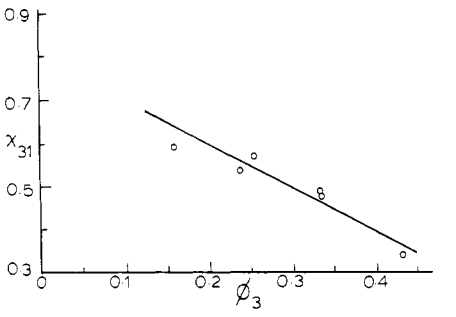

Figure 2. Concentration dependence of the χ parameter for the system $C_{10}H_{18}$/PS(80 000) as measured by vapor sorption experiments.

polymer blends.[25] A polymer–solvent solution is allowed to come to equilibrium with pure solvent of known partial pressure. As a first approximation, the activity of the solvent is equal to the relative vapor pressure P/P°, where P° is the vapor pressure of the pure solvent. For this study, the approximate activities were corrected for deviation from the perfect gas law by eq 1, where α and β

$$\ln a_3 - \ln (P/P^\circ) = (P - P^\circ)/[RT(\alpha/RT - \beta)] \quad (1)$$

are the two van der Waals constants. Since most of the paper deals exclusively with a binary mixture of polymers, we use the subscript 3 for the solvent. The activity coefficient a_3 of the solvent in a binary or ternary solution is related to the chemical potential $\Delta\mu_3$ by

$$\ln a_3 = \Delta\mu_3/RT \quad (2)$$

For a binary solution

$$\Delta\mu_3/RT = \ln \phi_3 + (1 - 1/r_1)\phi_1 + \chi_{31}\phi_1^2 \quad (3)$$

where ϕ_3 and ϕ_1 are the volume fractions of the solvent and the polymer with a degree of polymerization r_1, respectively. χ_{31} is the Flory/Huggins parameter. For a ternary solution we have[11,12]

$$\Delta\mu_3/RT = \ln \phi_3 + (1 - 1/r_1)\phi_1 + (1 - 1/r_2)\phi_2 + (\chi_{31}\phi_1 + \chi_{32}\phi_2)(1 - \phi_3) - \chi_{12}\phi_1\phi_2 \quad (4)$$

where subscript 3 refers to the solvent and subscripts 1 and 2 to the two polymers. The value of the Flory/Huggins parameter χ_{12} of the two polymers can be calculated from three separate vapor sorption experiments, one with each of the polymer components separately and a third with the blend.

Polymer–Solvent Systems. Two different molar mass polystyrene–decahydronaphthalene systems were investigated, PS(15 000) and PS(80 000). The vapor sorption measurements were made at 80 °C. The glass transition temperature is 100 °C for both samples of polystyrene. Once a certain amount of solvent has been absorbed, the polystyrene is sufficiently plasticized so that the experimental temperature is now above T_g and the system is no longer glassy. Equation 3 is used to evaluate the χ_{31} parameter from the equilibrium sorption data of the plasticized systems. Results are shown in Figures 1 and 2 for PS(15 000) and PS(80 000) respectively. The solid lines represent a linear least-squares analysis of the data. The results are

$$\chi_{31} = -1.00\phi_3 + 0.797 \quad \text{for PS(15 000)}$$
$$\chi_{31} = -0.565\phi_3 + 0.688 \quad \text{for PS(80 000)}$$

We notice that the molar mass of polystyrene has a considerable influence on the composition dependence of χ_{13} in the composition range investigated.

Vapor sorption measurements were also made on the decahydronaphthalene/PoClS system. The T_g for PoClS

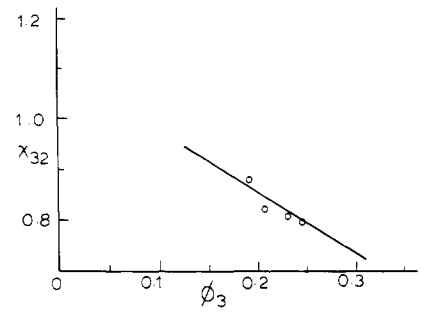

Figure 3. Concentration dependence of the χ parameter for the system $C_{10}H_{18}$/PoClS as measured by vapor sorption experiments.

Table I
Flory–Huggins Polymer–Polymer Parameter at 80 °C

% PS(15 000) in film	χ_{12}
75	0.31
	0.07
	0.35
	0.14
50	0.04
	0.23
	0.23
	0.08
25	−0.43
	−0.08
	−0.63
	−0.94

is 133 °C. Therefore, it is necessary for the polymer to absorb more solvent before the T_g is depressed below the experimental temperature of 80 °C. The χ_{32} parameter for the plasticized system is shown in Figure 3. The solid line is a linear least squares fit given by

$$\chi_{32} = -1.42\phi_3 + 1.144$$

Polymer–Polymer–Solvent Systems. Three different ternary systems were investigated; PS(15 000)/PoClS/decahydronaphthalene with polymer–polymer ratios of 25:75, 50:50, and 75:25. The blend of the high molar mass polystyrene is an immiscible system and eq 4 does not apply. The values of χ_{12}, calculated with eq 4, and the previously determined values of χ_{31} and χ_{32}, are shown in Table I. There is a considerable scatter in the χ_{12} values. Except for the 25:75 systems the values are small and positive, an indication for a possible absence of specific interactions. Since the Flory/Huggins parameters for the latter systems are found to be negative, it is difficult to draw a definite conclusion regarding the presence or absence of specific interactions. The results are, however, clearly different from those of various other miscible polymer system where unequivocally negative values are found for the χ parameter.[27,33-35] This indicates that there is a much stronger interaction between both components

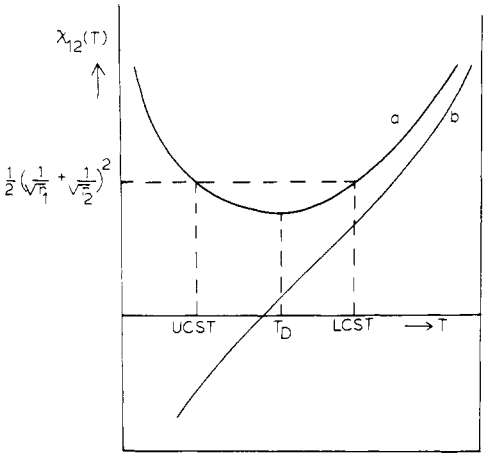

Figure 4. Schematic respresentation of the temperature dependence of the χ parameter without (a) and with (b) specific interaction.

of those blends than there is between polystyrene and poly(*o*-chlorostyrene).

The variation with composition of the χ parameter is in general attributed to a difference in surface/volume ratio of the two components.[13] This difference might be quite large for polymer–solvent systems. Our results on the polymer–solvent systems are in agreement with this viewpoint. Accordingly, for two polymers that are very much alike, one does not expect a significant composition dependence of the χ parameter as found for the PS-(15 000)/PoClS system. Although this dependence probably reduces somewhat for a higher molar mass of PS, it seems unlikely that it will become negligible. On the other hand one has to realize that there exists some doubt regarding the validity of the solution measurements as a basis for deriving the χ parameter of the solvent-free polymer blend.

Enthalpy of Mixing

In the preceding section the chemical potential instead of the free energy of mixing was taken as a starting point. If the Flory/Huggins parameter is independent of composition, one might as well start from the free energy of mixing, which for a binary mixture is given by the familiar expression of eq 5. For simplicity, we will from now on

$$\Delta G_M/RT = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \chi_{12}(T)\phi_1\phi_2 \quad (5)$$

restrict ourselves to this composition-independent case, although the results have a general validity as will be argued at various stages.

According to the equation of state theory[1,2] or the lattice fluid theory,[6] the χ parameter consists of two contributions, an exchange interaction term and a free-volume term. The former dominates the low-temperature behavior and is positive for dispersive forces and negative when specific interactions like weak hydrogen bonds or charge-transfer complexes are present. The free-volume contribution is positive and becomes increasingly important at higher temperatures. A well-known schematic respresentation for χ_{12} as a function of temperature is presented in Figure 4.[14,15] Clearly, the presence or absence of specific interactions creates two completely different situations.

The phase behavior is determined by the condition that, at constant pressure and temperature, the free energy of mixing is a minimum. From this it follows that phase separation occurs in such a way that the chemical potential of each component is equal in both phases. For a strictly binary system the critical points coincide with the extreme

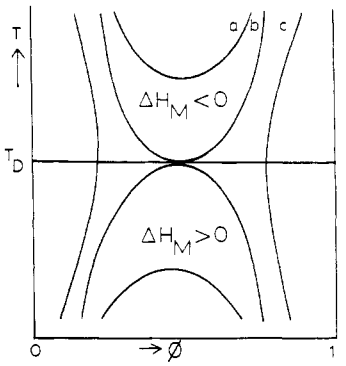

Figure 5. Schematic representation of the connection between the sign of the enthalpy of mixing and the position in the phase diagram.

of the coexistence curves. The critical conditions are given by

$$(\partial^2\Delta G_M/\partial\phi_2^2)_{P,T} = (\partial^3\Delta G_M/\partial\phi_2^3)_{P,T} = 0 \quad (6)$$

Together with eq 5 this results in the well-known expression for the critical value χ_c of χ_{12}:[11,12]

$$\chi_c = (r_1^{-1/2} + r_2^{-1/2})^2/2 \quad (7)$$

The system is miscible for all temperatures for which $\chi_{12}(T) < \chi_c$ and partially miscible for all temperatures for which $\chi_{12}(T) > \chi_c$. Figure 4 shows that UCST and LSCT are possible for dispersive forces, whereas for systems with specific interactions, like most miscible polymer blends, only LCST behavior is expected.

The enthalpy of mixing is related to the free energy of mixing by

$$\Delta H_M = \Delta G_M - T(\partial\Delta G_M/\partial T)_P \quad (8)$$

Using eq 5 this gives

$$\Delta H_M = -RT^2(\partial\chi_{12}/\partial T)\phi_1\phi_2 \quad (9)$$

The sign of the enthalpy of mixing is determined by the first derivative of the χ parameter.

Consider a binary system for which the $\chi_{12}(T)$ curve is given by curve a in Figure 4. Moreover, let us assume that $\chi_{12}(T)$ is independent of the molar mass of both components. If r_1 and r_2 are such that χ_c, given by eq 7, is larger than the minimum of the $\chi_{12}(T)$ curve, we have, as indicated in Figure 4, a UCST and an LCST at a temperature determined by $\chi_{12}(T) = \chi_c$. Increasing r_1 and/or r_2 decreases the value of χ_c until it finally coincides with the minimum of the $\chi_{12}(T)$ curve. The UCST and the LCST merge in a critical double point (CDP) at the temperature T_D for which $\chi_{12}(T)$ is minimal. According to eq 9, this means $\Delta H_M > 0$ for $T < T_D$, $\Delta H_M = 0$ for $T = T_D$, and $\Delta H_M < 0$ for $T > T_D$. Figure 5 represents the phase diagram as it follows from the above considerations.

Ryan[9] measured the enthalpy of mixing at 35 and 68 °C for PS and PoClS for various molar masses of PS and a fixed molar mass of PoClS. He varied the number-average molar mass of PS from 9000 to 50 000. The number-average molar mass of PoClS was about 50 000 and the weight-average molar mass about 100 000. In nearly all cases a small but positive heat of mixing was found, with no clear dependence on the molar mass of PS. This shows that 35 and 68 °C are in the temperature range in which a UCST is possible. Consequently, blends of PS and PoClS constitute an example of miscibility without specific interactions. McMaster[8] already showed that this exceptional situation can occur provided the exchange interaction contribution is sufficiently small and provided the

P–V–T properties of both components do not differ too much.

As mentioned in the introduction, Ryan[9] also showed that the PS(26 700)/PoClS system is miscible in the temperature range from 150 to 400 °C, whereas the PS-(30 400)/PoClS system is only partially miscible in this region. Hence, curve c of Figure 5 is characteristic for blends with PS having a molar mass exceeding 30 400 and curve a for blends with PS having a molar mass smaller than 26 400.

To arrive at these conclusions we assumed that the χ parameter is independent of molar mass and composition. The former assumption, however, needs only to hold for a molar mass varying between 26 700 and 30 400, which is, even without experimental evidence, a reasonable approximation. Moreover, if χ_{12} is ϕ dependent, Prigogine and Defay[16] showed that ΔH_M is negative near an LCST and positive near a UCST, unless an inflection point exists in the composition dependence of ΔH_M. Although this cannot be precluded in general, it is unlikely and to our knowledge none has been reported along the critical isotherm. An alternative derivation of this result has been given by Rowlinson[29] and Sanchez.[30] A crucial assumption in all these treatments is the possibility of an expansion of the free energy in a Taylor series at the critical point. It is, however, generally recognized that the thermodynamic quantities depend nonanalytically on their variables at the critical point.[31] It can be shown that the aforementioned connection between the sign of the enthalpy of mixing and the type of phase behavior also follows from the modern theory of critical phenomena.[32]

Molar Mass Dependence. The sensitivity of the phase behavior to a change in molar mass is related to the shape of the $\chi_{12}(T)$ curve. A very flat shape, as near a critical double point in polymer blends, will result in a large change in LCST and UCST for a small change in molar mass of one or both components. Consider for simplicity a system of two polymers of equal degree of polymerization, r. The critical value of χ_{12}

$$\chi_c = 2/r \tag{10}$$

follows from eq 7. Suppose T_c is the corresponding critical temperature (UCST, LCST, or CDP). A small change in T_c to T_{c1} due to a change in degree of polymerization from r to r_1 corresponds to a critical value of χ_{12} given by

$$\chi_{12}(T_{c1}) = \chi_{12}(T_c) + (T_{c1} - T_c)\chi'_{12}(T_c) + \frac{(T_{c1} - T_c)^2}{2}\chi''_{12}(T_c) + \dots \tag{11}$$

If the starting point is the critical double point temperature T_D we find, combining eq 10 and 11 [$\chi'_{12}(T_D) = 0$],

$$T_{c1} - T_D = \frac{2}{\chi''_{12}(T_D)^{1/2}}\left(\frac{r - r_1}{rr_1}\right)^{1/2} \tag{12}$$

Similarly, if T_c is sufficiently far from the critical double point,

$$T_{c1} - T_c = \frac{2}{\chi'_{12}(T_c)}\frac{r - r_1}{rr_1} \tag{13}$$

The critical temperature is, according to eq 12, very sensitive to the difference $r - r_1$ near the critical double point provided $\chi''_{12}(T_D)$ is small. In this respect it is also important to note that the factor $(r - r_1)/rr_1$, which is small for a small difference between r and r_1, occurs with the power 1/2. Away from the critical double point eq 13 holds. The sensitivity is now determined by the first derivative $\chi'_{12}(T_c)$, and only if it is small does a small change in degree of polymerization lead to a large change in critical temperature. If χ'_{12} is a sufficiently fast increasing function of $|T - T_D|$, this is only true near the critical double point.

The critical double point is seen to play a different role as far as the power of the factor $(r - r_1)/rr_1$ is concerned. A similar phenomenon is found for the critical exponent β, which describes the shape of the co-existence curve at the critical point. At the critical double point this exponent is doubled compared to its value at ordinary critical points. This result is generally valid, but can easily be proven within the framework of mean field theory.[17]

The foregoing analysis cannot simply be extended to systems where the Flory/Huggins parameter depends strongly on composition. As stated before, theoretically one does not expect this to be true for polymer blends consisting of polymers that are very similar. The experimental results for the PS(15 000)/PoClS system indicate, however, that the situation might be more complicated. Nevertheless we do not expect this to alter the above conclusions significantly. For polymer–solution systems on the other hand the first derivative of the Flory/Huggins parameter with respect to temperature is, due to the large differences between a polymer and a solvent, much larger than for polymer–polymer systems with a critical double point. The enhanced sensitivity will presumably be less. This is confirmed by the existing data for the polystyrene–acetone system.[18]

Model Calculation. The analysis so far showed that the experimental results for PS/PoClS blends clearly point to the possibility of critical double points in these systems. Although we argued that the enhanced sensitivity of the phase behavior to a change in molar mass is probably due to this fact, it is not clear yet whether such a small change can indeed create a miscibility region of over 250 °C. An obvious model to investigate this is given by Flory's equation of state theory.[1,2]

The starting point for this theory is an assumption of Prigogine[19] that the degrees of freedom of a molecule in a liquid can be separated into internal and external degrees of freedom. Generally, $3c$ ($c < 1$) is used to denote the number of external degrees of freedom per segment. The intersegmental energy arises from interactions between surfaces of adjoining segments. The mean intermolecular energy is taken to be inversely proportional to volume. For a system consisting of molecules of r segments the equation of state

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{14}$$

can be derived: where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{v} = v/v^*$. It follows from eq 14 that the characteristic quantities P^*, T^*, and v^* are related to the thermal expansion coefficient α, the volume per segment v, and the thermal pressure coefficient γ. At atmospheric pressure, these relations are

$$\tilde{v} = \{1 + \alpha T/[3(1 + \alpha T)]\}^3 \tag{15}$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{16}$$

$$P^* = \gamma T \tilde{v}^2 \tag{17}$$

The adaptation to mixtures is based on the assumption of random mixing of the different segments, which are chosen to have equal hard core volume v^*. The exchange interaction is described by an interaction parameter X_{12}. This leads to an equation of state for the mixture in a form identical with eq 14 if the characteristic quantities for the mixture are defined by

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1\theta_2 X_{12} \tag{18}$$

$$\tilde{T} = T/T^* = (1/P^*)(\phi_1\tilde{T}_1 P^*_1 + \phi_2\tilde{T}_2 P^*_2) \tag{19}$$

Table II
Pure Component Properties at 200 °C[a]

component	v_{sp}, cm³/g	$\alpha \times 10^4$, K⁻¹	γ, cal/(cm³ K)	P^*, cal/cm³	T^*, K	v^*_{sp}, cm³/g	$\bar{M}_w$
1	1.033	5.80	0.167	120	8679	0.839	variable
2	0.877	6.30	0.157	116	8301	0.706	100 000

[a] Mixture properties: $s_1/s_2 = 1$, $X_{12} = 0.0225$.

where ϕ_1 and ϕ_2 denote the segment fraction of components 1 and 2, respectively, and θ_2 is the surface fraction of component 2. Several other parameters have been introduced, but they will be ignored in this study.

The equation for the spinodal of a binary mixture is, in the low pressure approximation, given by eq 20.[20] This

$$1/r_1\phi_1 + 1/r_2\phi_2 - (2v^*/kT)(s_2/s)^2(s_1/s)X_{12}/\tilde{v} - \left(\frac{\partial\tilde{v}}{\partial\phi_1}\right)_{P,T}\{[c_1 - c_2]/\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1) - v^*/kT\tilde{v}^2[P^*_1 - P^*_2 - (s_2/s)(\phi_2 - \theta_1)X_{12}]\} = 0 \quad (20)$$

expression differs from the one used before by the omission of the kinetic energy related contributions. (The appropriate form of the partition function, from which an expression for the spinodal can be derived, is a rather involved problem; details can be found in ref 28.)

Identifying the expression for the chemical potential of component 1, as given by the equation of state theory, with eq 3 gives the following connection between the Flory/Huggins parameter χ_{12} and X_{12}:[1]

$$\chi_{12} = (3c_1/\phi_2^2)\ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (v^*/kT\phi_2^2)[P^*_1(1/\tilde{v}_1 - 1/\tilde{v}) + \theta_2^2X_{12}/\tilde{v}] \quad (21)$$

The expression for the enthalpy of mixing finally is given by[2]

$$\Delta H_M/(r_1N_1 + r_2N_2)v^* = \phi_1P^*_1(1/\tilde{v}_1 - 1/\tilde{v}) + \phi_2P^*_2(1/\tilde{v}_2 - 1/\tilde{v}) + (\phi_1\theta_2/\tilde{v})X_{12} \quad (22)$$

It is clear from the foregoing that the application of the equation of state theory requires v_{sp}, α, and γ. The P–V–T properties of polystyrene have been investigated by many authors. In contrast, no data, with the exception of the specific volume, are available for poly(*o*-chlorostyrene). The equation of state parameters used for component 1 are those for PS as determined by Hocker et al.[21] The coefficient of thermal expansion and the thermal pressure coefficient of component 2 are chosen to be 5–10% different from those of component 1, a choice motivated by McMaster's conclusion that a UCST in polymer blends is only possible if α and γ of both components are very similar. The specific volume of component 2 is derived from the literature data for PoClS.[22] The weight-average molar mass of component 2 is kept fixed during the calculations and is equal to that of the PoClS used by Ryan in his T_g measurements. The molar mass of component 1 is varied. As is well-known, the equation for the spinodal of a mixture of polydisperse polymers is, under certain assumptions, the same as for a mixture of monodisperse polymers provided the weight-average chain lengths are used.[8,23]

In addition to the equation of state data for the pure components, the segment surface ratio is required for the characterization of the mixture. There are essentially two methods to calculate this ratio, Flory's method[2] based on the approximation of polymer segments by cylinders or the estimation using the group surface areas and volumes given by Bondi.[24] Both methods lead, for the PS/PoClS system, to a value of approximately unity. This choice for s_1/s_2 of our model system implies also that χ_{12} calculated by eq 21 will depend only slightly on composition. To completely characterize the model system, the exchange interaction parameter has still to be determined. It is chosen in such a way that a critical double point occurs inside the experimental temperature range for a molar mass of PS of about 31 000. A suitable choice appears to be $X_{12} = 0.0225$ cal/cm³. All the data are collected in Table II.

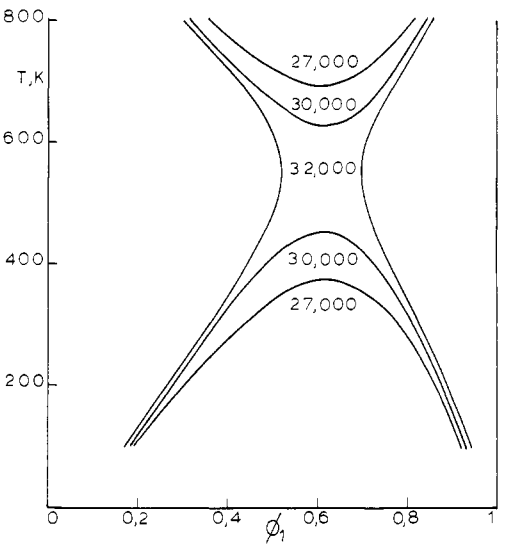

Figure 6. Simulated spinodals for the PS/PoClS system for the indicated molar mass of polystyrene.

The simulated spinodals for polystyrene of various molar masses are shown in Figure 6. The extrema of the spinodals are located in the polystyrene-rich region of the phase diagram. This is to be expected since polystyrene is the lower molar mass component. As Figure 6 illustrates, the blends with polystyrene of molar mass 32 000 or greater have an hourglass-shaped spinodal. When the molar mass of the polystyrene is dropped by only 2000, the blend is now miscible for all compositions between approximately 450 and 630 K. A further reduction to PS(27 000) results in an UCST at 370 K and a LCST at 700 K. The LCST is now above the degradation temperature of the two components and therefore cannot be determined experimentally. The UCST is below the T_g of the polymer blend. Figure 6 demonstrates that under the right circumstances the equation of state theory is capable of predicting the type of mixing behavior that has been proposed for the PS/PoClS system.

The situation is more clearly illustrated in Figure 7. This shows the temperature dependence of χ_{12} for a fixed segment fraction $\phi_1 = 0.5$. Since the dependence of χ_{12} on composition is extremely small, every other choice of ϕ_1 would have resulted in approximately the same figure. The critical value of χ_{12} is still in a very good approximation given by eq 7. The horizontal lines in Figure 7 represent the critical value for χ_{12} for polystyrene having the indicated molar mass. It is easy to see that the flatness of the χ_{12} vs. T curve in the vicinity of the critical double point is, as predicted by eq 12 and 13, responsible for the large temperature change in the critical temperatures with very small changes in molar mass.

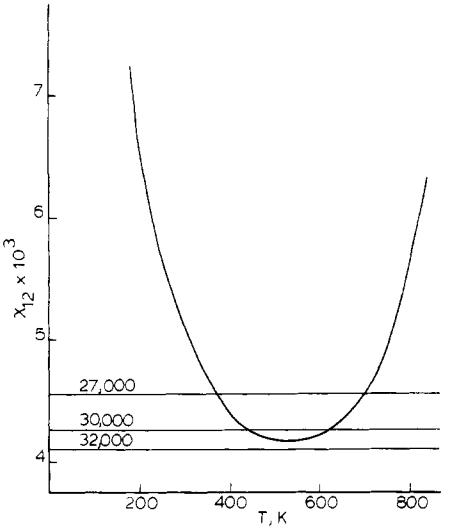

Figure 7. Calculated temperature dependence of the χ parameter for the PS/PoClS system. The horizontal lines represent the critical values of the χ parameter for the indicated molar mass of polystyrene.

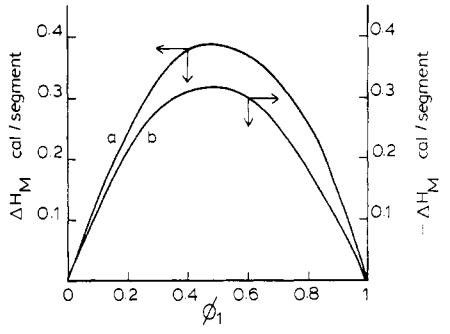

Figure 8. Calculated enthalpy of mixing of the PS/PoClS system for 300 K (a) and 600 K (b).

The predicted values of the enthalpy of mixing in calories/segment are shown in Figure 8. The values are extremely small but, in accordance with previous statements, they are positive below T_D and negative above T_D.

It must be reemphasized that all predictions of the equation of state theory presented for the PS/PoClS blends have been based on estimated equation of state parameters for PoClS. These predictions are intended to give a qualitative picture of the mixing behavior of the polymer blend. The numbers are significant only in terms of their relative magnitudes and signs.

Concluding Remarks

Most experimental observations on PS/PoClS blends point to the existence of critical double points in these systems. The application of the equation of state theory, in particular, shows the connection between the occurrence of a critical double point and the enhanced sensitivity of the phase behavior with respect to a small change in molar mass. The calculated values for the enthalpy of mixing are also in qualitative agreement with experimental findings. However, the absolute values are an order of magnitude smaller than the observed ones. Part, but certainly not all, may be attributed to the use of more or less arbitrary P–V–T data for PoClS. Another source for deviation could be the polydispersity, since there are many indications that the equation of state theory, in the form used here, does not take this properly into account.[26]

The calculated values for the χ parameter are, due to the choice of $s_1/s_2 = 1$, nearly independent of composition, whereas the experimental values for the PS(15000)/PoClS blends based on vapor sorption measurements showed an unexpected composition dependence. To investigate more thoroughly the behavior of the χ parameter as a function of molar mass and composition, future studies with a different solvent are planned. Because decahydronaphthalene is a very high-boiling solvent and a bad plasticizer, it was necessary to perform the vapor studies at an elevated temperature in order to get sufficiently high vapor pressures to permit enough sorption of vapors into the polymers. Temperature control proved very difficult. Use of a better plasticizer, criteria for which are discussed in ref 36 and 37, with a lower boiling point would probably greatly reduce the error in these measurements.

Acknowledgment. This work was supported by AFOSR Grant 81-0101.

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